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THE TEMPERATURE FORMULA OF THE WESTON STANDARD CELL.*

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INTRODUCTION.

The more recent work on the standard cell has demonstrated that the Clark and Weston types are both reproducible to a very high degree of accuracy, and that when properly set up both may be depended on within a few parts in 100,000 for a year at least. As these qualities, in connection with the concreteness and ease of reproduction of the standard cell, seem to point to it as the logical choice for the second fundamental electrical unit, a redetermination of the temperature formulæ has been undertaken. On account of the very small effect of temperature variations on its electromotive force and the absence of cracking at the amalgam terminal, distinct advantages over the Clark cell, an investigation of the Weston cell was first made. A redetermination of the temperature formula of the Clark cell will, however, also be undertaken.

HISTORICAL REVIEW.

The first statement regarding the temperature coefficient of the Weston cell is found in the specifications of the patent issued to Dr. Edward Weston, who justly claimed as a special advantage of the cell its very small variation in electromotive force with temperature changes.

The results of Dearlove,[1] obtained with several lots of cells in which apparently no excess of cadmium sulphate or mercurous sul-

*Read at meeting of American Electrochemical Society, Apr. 30, 1908. Trans., **13**, p. 187.

[1] Electrician, **31**, p. 645; 1893.

phate was employed, were quite irregular. Three cells of the first lot, in which the amalgam "was estimated to contain one part of cadmium to five parts of mercury," had an E. M. F. greater than 1.03 volts, and differed from each other by as much as 2 millivolts. In addition the E. M. F. of the cells was variable, and all had abnormally high temperature coefficients. The irregularities were attributed by Dearlove to the amalgam, the composition of which was found by him to exert a very decided influence on the E. M. F. Five cells set up with 12.5 per cent amalgam in 1893 gave a temperature coefficient ranging between 0.003 and 0.007 per cent per degree in the interval between 15° and 35°, and 0.007 to 0.010 per cent between 15° and 64°. Observations made while the cells were being brought back to room temperature and others on cooling to 0° showed that the results were influenced by marked hysteresis. Seven presumably similar cells set up by Dr. Muirhead were found by Dearlove to have a "temporary temperature coefficient" of 0.008 per cent between 2°.5 and 22°.

The generally accepted temperature formula for the Weston cell with excess of cadmium sulphate crystals, which alone will be considered in this paper, is based on a series of measurements by Jaeger and Wachsmuth,[2] extending over a period of five days, during which the four cells employed were subjected to large and sudden temperature changes, no attempt being made to maintain the temperature constant for any considerable time. Besides the comparisons made at room temperature, 30 measurements in terms of two additional cells employed as reference standards are given, which may be summarized as follows:

On the first day two of the four cells were measured at 14°.9; on the following day the same cells were compared with each other at the same temperature. On the third day one cell was measured at 0° and two others at 9°, 9°.1, and 9°.6. During the forenoon of the fourth day two cells at 1°.7 and two at 12°.6 and 12°.8 were compared with the reference cells, while during the afternoon two sets of measurements were made at 25°.3 and 25°.9 on one cell of each lot. On the fifth day one cell at 1°.5 and two at 20° were

[2] Wied. Ann., **59**, p. 575; 1896. Elektrotechn. Zs., **15**, p. 507; 1894.

measured. Additional observations not given in the paper, and presumably check measurements at the above temperatures, are referred to in a footnote.

The cells in question were all made up with 14.3 per cent amalgam, with which irregularities observed at lower temperatures have since been connected. The following formula was derived from *all* of the observations:

$$E_t = E_{20} - .000038\ (t-20) - .00000065\ (t-20)^2$$

This formula has since been in general use. On account of irregularities observed between 0° and 5°, the authors limited its application to temperatures between 5° and 26°, and still later Jaeger[3] raised the lower limit to 10°.

These irregularities were first attributed by Kohnstamm and Cohen[4] to an inversion of cadmium sulphate similar to that observed in the case of zinc sulphate in the Clark cell, but it may be regarded as now established that no such inversion takes place between 0° and 60°. Irregularities have, however, been shown to be introduced by the employment of cadmium amalgams containing more than 15 per cent by weight of cadmium. Jaeger[5] found that at room temperatures the E. M. F. of the Weston cell is almost independent of the composition of the amalgam employed, provided it contains between 5 and 14.3 per cent cadmium. In the case of more concentrated amalgams the E. M. F. was found to be variable, the changes amounting to 1 millivolt for a 15.4 per cent amalgam, 11 millivolts for a 20 per cent amalgam, and 44 millivolts for amalgamated cadmium rods. Jaeger, therefore, recommended the use of a somewhat more dilute amalgam than that first employed, since its composition was too close to the limit at which irregularities were observed. No observations were, however, made by Jaeger at other than room temperatures. The subject has been further investigated by Bijl[6] and Puschin,[7] and it has been shown that cadmium amalgams consist, within certain temperature limits, of a liquid phase and a solid

[3] Zs. Instk., **20**, p. 317; 1900. Ann. d. Phys., **4**, p. 123; 1901.
[4] Wied. Ann., **65**, p. 344; 1898.
[5] Wied. Ann., **65**, p. 106; 1898.
[6] Zs. f. Phys. Chem., **41**, p. 641; 1902.
[7] Zs. Anorg. Chem., **36**, p. 201; 1903.

phase, the latter composed of mixed crystals of cadmium and mercury, having a composition depending on the temperature. With both phases coexistent the E. M. F. toward cadmium sulphate at a given temperature is, therefore, independent of the relative amounts of the metals present, as found by Jaeger, while in the absence of the liquid phase irregularities in behavior are found. The composition of the amalgam to be employed in the standard cell must therefore be such that both the liquid and solid phases will be present within the usual temperature range, a condition probably satisfied by the 12.5 per cent amalgam employed at the Bureau of Standards and elsewhere.

A temperature coefficient more than twice as large as that obtained by Jaeger and Wachsmuth was found by Barnes,[8] who measured three cells set up with 1 : 6 amalgam, two of which were filled with moist cadmium sulphate crystals instead of crystals and solution. Measurements were made between 0° and 40° "allowing ample time at each interval for the establishment of a steady and uniform temperature." The observations at the various temperatures were completed in one day, the cells having been kept at 0° during the night previous. The values obtained above 15° were fairly well represented by a linear coefficient of 0.0086 per cent per degree, but under 15° Barnes states that no regularity can be said to exist, the difference between 0° and 15° being 2.1, 4.3, and 3.6 millivolts. From the observations made immediately before and after the above measurements, changes of + .11, − 0.35, and + 0.21 millivolt were found for the cells, indicating that trustworthy results are hardly to be expected after the relatively rapid temperature changes on account of hysteresis. Large differences were also found by Barnes in the values of four other cells rapidly brought from 15° to 0°.

A further study of all the Reichsanstalt cells with 1 : 6 amalgam was made by Jaeger[9] in 1896, but the results were not published until after the appearance of Barnes's paper. Thirty-four cells were measured in an oil bath at 0°, at which temperature 14 were found to differ from the values calculated by the formula of Jaeger and Wachsmuth by less than 0.02 per cent, while the observed values of

[8] Jour. Phys. Chem., 4, p. 339; 1900.
[9] Ann. d. Phys., 4, p. 123; 1901.

the remaining 20 were from 0.02 to 0.23 per cent (mean, 0.09 per cent) too high. The observations were made several hours after the bath had been cooled to 0°. In addition, three of the cells, one belonging to the first group and two to the second, were measured at temperatures between −16°, the freezing point of saturated cadmium sulphate solution, and 40°. The two "abnormal" cells showed maximum differences from the temperature formula of +4.5 and +3.2 millivolts, while the cell with "normal" behavior showed a maximum difference of −0.57 millivolt (at −11°.5). The observations extended over a period of two weeks, during which the cells were generally allowed to come to room temperature overnight. After the first observation on each day, usually at room temperature, the cells were subjected to relatively large temperature changes. An inspection of the tables and the plotted results, particularly consecutive measurements on the same day, in which the temperature was changing slowly after a relatively large change, seems to indicate that the discrepancies are due to hysteresis.

A very extensive series of observations between 0° and 30° was made by Jaeger and Lindeck[10] in 1899, with the object of verifying the formula obtained by Jaeger and Wachsmuth. Fifty-six series of measurements were made on eight old cells with 14.3 per cent amalgam and twelve new cells with 13 per cent amalgam, together with five unsaturated Weston cells and five Clark cells with which we are at present not concerned. Six of the old Weston cells had already been classed by Jaeger as abnormal at lower temperatures, while the two others had apparently not been previously investigated at such temperatures. As might have been expected, these all showed very marked irregularities, particularly at 0°, at which all the cells were kept for two periods of eight and eleven days, twenty-three series of measurements being made. The new cells, however, showed much smaller changes under these conditions. A second series of measurements was later made on five cells with 13 per cent amalgam, set up at the same time as the twelve above referred to, and on two lots of twenty new cells set up with 12 and 13 per cent amalgam. The results obtained at the Reichsanstalt will be discussed below in their relation to those found in the present investi-

[10] Zs. Instk., **21**, p. 33 and p. 65; 1901. Ann. d. Phys., **5**, p. 1; 1901.

gation, particularly as the data obtained by Jaeger and Lindeck were not employed in the derivation of a temperature formula, being merely used for verifying the previous work at the Reichsanstalt.

Two further series of measurements by Barnes and Lucas[11] on four new "moist crystal" cells are summarized below. In the published tables only the uncorrected potentiometer readings are given, so that the reductions were made on the assumption that the values of two portable cells of the Weston Electrical Instrument Company, measured at the same time, were the same for both sets of observations.

TABLE I.

Results of Barnes and Lucas.

Cells	Series	Temperature range	Mean temperature coefficient		
			Observed	Range	Calculated
Cd 16	1	14°6–27°9	— .0050%	.0045– .0057%	— .0040%
17		14°6–19°9	.0030	.0024– .0030	.0035
18		19°9–27°9	.0064	.0064– .0081	.0043
19					
Cd 16	2	13°6–29°5	— .0058	.0057– .0060	— .0040
17		13°6–18°7	.0024	.0020– .0028	.0033
18		18°7–29°5	.0075	.0070– .0078	.0044

It will be seen that the results can not be represented by a linear temperature coefficient; that the differences in temperature coefficient between the individual cells are large, and that the values for the lower range are *smaller* than those called for by the generally accepted temperature formula (column 6). The results can, therefore, not be regarded as confirming the previous work of Barnes as to the temperature coefficient being linear, nor do they establish the opinion expressed by Barnes that the differences in results are due to the greater rapidity with which saturation equilibrium is established in the case of the "moist crystal" cells in comparison with cells of the usual construction.

[11] Jour. Phys. Chem., 8, p. 196; 1904.

Smith[12] at the English National Physical Laboratory has recently found, as the result of measurements on six selected cells between 10° and 30°, the formula:

$$E_t = E_{17} - 0.0000345\,(t-17) - 0.00000066\,(t-17)^2$$

The temperature was changed at the rate of 1° per hour and maintained constant by means of a thermo-regulator at least one hour before the measurements were made, the cycle of temperatures being repeated three times. The data on which the formula is based are not published, but judging from the results obtained at the Bureau on cells obtained by exchange from the National Physical Laboratory, some hysteresis may be expected under the above conditions. On account of the close agreement, in the range covered, of Smith's formula with that of the Reichsanstalt, the universal adoption of the latter is recommended by him.

THE PRESENT INVESTIGATION.

The Cells.—In the present investigation it was thought desirable to include a large number of cells, so as to determine whether any differences in the temperature coefficient are introduced by variations in the methods of preparation and purification of the materials. Altogether 200 cells were studied, including nearly all those previously reported on,[13] a number of exchange cells obtained from other investigators, and a considerable number of other cells set up at the Bureau to determine the influence of variations in the specifications which might possibly affect the E. M. F.

The Comparing Baths.—The cells were contained in two automatically regulated petroleum baths, each provided with an efficient stirrer, a thermo-regulator sensitive to within 0°.01 C, resistance coils for electric heating, and coils for water circulation for temperatures below that of the room. As described in the article referred to, the cells were mounted in such a way as to be free from direct influence of the heating or cooling coils. The oil in which the cells were immersed covered them to a depth of several centimeters.

The Temperature Cycle.—The measurements were made at every 5° for a complete cycle from 0° to 40°, beginning and ending at

[12] Phil. Trans. Roy. Soc., **207**, p. 411; 1908.

[13] Wolff and Waters, this Bulletin, **4**, p. 1; 1907. (Reprint No. 70.)

25°, the lower temperatures being taken first, and a smaller cycle from 15° to 25°. As it was deemed desirable to repeat the 0° measurements with ascending temperatures, both baths were maintained at a temperature of approximately −4° for twenty-four hours between the two series of observations made at 0°. The regulator was set so that the temperature at which the baths regulated was within ± 0°.02 of the temperature desired, except for 10 sets in bath 1 and 4 sets in bath 2, so that, by applying a slight correction, the values observed could be reduced to the temperatures decided upon, thus making possible the application of a least-squares formula to the reduction of the results.

Regulation.—The temperature of the baths was maintained constant well within 0°.02 C for at least forty hours at each temperature. No difficulty was of course experienced in regulating the baths at temperatures above that of the room (about 23°), but at 20° and 15° great difficulty was at first found, mainly on account of the cooling coils of both baths being in parallel. In the first measurements at these temperatures the cooling was effected by a very slow stream of tap water which had been passed through a lead coil surrounded by crushed ice. (The use of ice, even for these temperatures, was made necessary on account of the temperature of the tap water rising above 20° during the night.) The difficulty was traced to the separation of air bubbles from the water, which, collecting in the cooling coils, gradually obstructed the circulation and thus disturbed the regulation. Various schemes were tried, but the most satisfactory method consisted in pumping water from a tank maintained several degrees below the temperature at which the baths were to be regulated. For this purpose a slow flow of ice water into the tank sufficed, the level being maintained by means of an overflow. A direct circulation of ice water was employed for the auxiliary cooling at 10°, while the lower temperatures, 5°, 0°, and −4°, were obtained by circulating a brine solution of suitable concentration, the brine being kept approximately at its freezing point by means of a coil in the same tank through which much cooler brine was circulated at a desired rate by the aid of a by-pass. In the few cases of defective regulation, occasioned by the separation of air bubbles, broken belts, etc., a new start was made and the cells were maintained at the desired temperatures for at least forty hours longer.

Method of Observation.—As the apparatus and method of observation have already been fully described,[14] only an outline will be here given. Each of the 200 cells was measured in opposition to a particular cell in a separate bath maintained at 25°. The latter was compared in a similar manner with 14 cells in the same bath, composing two sets of 7 to which all the results were reduced. In addition, the 7 cells of one of the reference sets, connected in series, were directly compared by the opposition method with five sets of 7 cells in each of the two baths. The slight differences found by the two methods, averaging ±2 microvolts per cell, exceeded 3 microvolts in only ten series.

Altogether 58 observations were made on each of the 200 cells, and 19 others kept at 25° in completing the two cycles. At each step at least two series of measurements were made, the first on the day after the temperature was changed, and the last after the cells had been at constant temperature at least 40 hours.

Including the series measurements over 12,000 separate observations were therefore made, about 3500 being employed in the calculations for the cells tabulated below.

Temperature Measurements.—On account of the relatively small temperature coefficient of the Weston cell all temperature measurements were made with sufficient accuracy by means of mercurial thermometers, graduated to tenths of a degree, for which the corrections were determined to 0°.01 by another division of the Bureau.

Reduction of Results.—In working up the results three corrections were applied to each observation. The first to reduce all results to a common basis, the mean value of the reference cells; the second to allow for the very slight temperature differences of the baths from their nominal values, and the third one-half the mean difference found by comparing the cells separately and in sets of seven in series. The two latter corrections rarely exceeded 2 microvolts.

A preliminary temperature formula was first calculated by the least-squares method from the means of all the observations on 10 cells selected on account of their small hysteresis as indicated by the agreement of the observations with ascending and descending

[14] Wolff and Waters, this Bulletin, **4**, p. 39; 1907.

temperatures. Although these values agreed within 5 microvolts of each other it was found that they could not be represented as well as might be expected by a quadratic formula. A three-term formula was therefore tried, which was found to give residuals of ± 2 microvolts. With the approximate temperature formula thus found,

$$E_t = E_{20} - 0.0000406\,(t - 20) - 0.000000939\,(t - 20)^2 + 0.000000009\,(t - 20)^3$$

the residuals for each cell at each temperature could be computed, and from these, corrections to the above coefficients for the individual cells were obtained. The residuals found at each temperature for the ten cells by the employment of the corrected coefficients thus obtained agreed with each other to within ±2 microvolts. This, with the close agreement of the third-term coefficients of the individual cells, seemed to fully justify the use of a three-term formula.

The results for a considerable number of cells were worked up by taking into account all the observations made, but an inspection of the latter indicated the presence of hysteresis in some of the cells, successive readings at the same temperature, in ascending and descending portions of the cycle, in both cases approaching the same common value, as was shown also in a preliminary study of some of the cells when subjected to rapid as well as prolonged temperature changes. It was therefore thought best to reject all but the last measurements made at each step of the temperature cycle. These measurements, made at least 40 hours after the temperature was changed by 5°, were given equal weight in computing the corrections to the coefficients of the trial formula.

DISCUSSION OF THE RESULTS.

In Tables II to VIII below the results for 178 of the 200 cells are given. The 22 omitted are made up of 7 exchange cells, 5 cells containing oil admitted through defective seals, 8 cells of a series set up to determine possible electromotive differences with samples of cadmium sulphate obtained from different sources and purified by different methods, together with 2 cells set up with white

mercurous sulphate paste which had been employed in special cells,[15] constructed to make possible a study of the influence of a thorough and continuous mixing of the ingredients of the paste by rotation of the cell about its axis. In all these cases the differences between the values obtained with ascending and descending temperatures were very large and irregular, and in addition the majority exhibited abnormal values before beginning the temperature cycle. The results seem to indicate a lag in the establishment of concentration equilibrium of the mercury ions, as abnormally high values are obtained at lower temperatures. This behavior is particularly marked in the cells set up to determine differences in the electromotive properties of different samples of cadmium sulphate, in which, in order to eliminate differences arising from the mercurous sulphate, relatively small quantities of this material had to be employed, owing to the supply of the particular sample being limited. The paste, in most cases, therefore, contained a relatively large excess of cadmium sulphate crystals. In two of the exchange cells set up at the University of Wisconsin, and which also exhibited abnormal and variable values before beginning the temperature cycle, there does not appear to be an excess of cadmium sulphate crystals in the paste. Among the other exchange cells excluded are one of the two obtained from the Reichsanstalt, in both of which the paste was probably disturbed in transit, two cells obtained from the National Physical Laboratory in 1904, and two set up by Prof. Hulett, in both of which oil was admitted through defective seals. All these cells exhibited abnormal values, particular attention being called to the behavior of F–7, set up by Prof. Hulett in 1904, and which belonged to the series, the behavior of which led him to suspect that the chemical system of the Weston cell is in unstable equilibrium.

In the following tables the cells are grouped according to the method of preparation or treatment of the mercurous sulphate employed in the cell.[16] Column 1 gives the number of the cell; column 2 the designation of the sample, the letter indicating the method employed; column 3, the mean of the total range in value of each cell

[15] Wolff and Waters, this Bull., 4, p. 81; 1907.

[16] This Bulletin, 4, p. 41; 1907.

at each temperature, all observations being included; column 4, the mean range, rejecting all but the last measurements of each set at each temperature; column 5, the maximum range corresponding to column 4; column 6, the square root of the mean squares of the residuals obtained from the temperature formula deduced for the particular cell, and columns 7, 8, and 9, corrections[17] in microvolts to be applied algebraically to the coefficients of the final formula given below.

TABLE II.

Cells Set Up with Electrolytic Mercurous Sulphate Made with Old Apparatus.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
*75	a_1	75	37.2	100	11.2	+ 8.02	−.037	−.0034
*76	a_4	23	8.3	17	2.6	+ 1.55	−.026	+.0005
77	a'_4	7	2.6	7	1.1	− .50	−.054	+.0028
*64	a_5	50	22.5	66	7.2	+ 4.23	−.047	+.0006
*65	a_6	27	12.8	30	3.1	+ 1.98	−.026	+.0010
*40	a_7	127	63.3	145	.....	+19.67	−.463	−.0209
*8a	a_7	99	58.3	100	13.0	+ 6.15	+.062	−.0048
*66	a'_7	33	13.7	39	4.1	+ 2.30	−.014	+.0010
*41	a_8	84	38.6	82	8.5	+ 5.28	−.079	+.0010
*9a	a_8	42	26.2	48	8.8	+ 2.20	+.057	−.0038
67	a'_8	20	8.5	20	11.0	+ 1.31	−.005	−.0024
*42	a_9	52	35.0	46	7.2	+ 3.35	+.008	−.0010
11a	a_9	11	2.4	4	1.9	+ .79	−.018	+.0002
68	a_{10}	21	9.5	20	3.0	+ 1.29	−.016	+.0007
70	a'_{10}	6	4.2	9	2.4	− .56	+.004	+.0008
71	a_{11}	6	3.2	9	2.7	− .44	+.015	.0000
*72	a'_{11}	28	12.9	25	3.1	+ 1.62	+.019	+.0008
73	a_{12}	7	3.0	5	2.4	− .03	−.001	+.0008
74	a_{13}	14	10.0	20	2.3	− .26	+.012	+.0007
110	a_{13}	7	2.8	10	1.4	− .45	+.010	+.0002
112	a_{13}	14	9.6	11	1.8	− .09	.000	.0000
173	a_{13}	4	2.0	4	1.7	− .65	+.006	+.0004

* Excluded in taking means.

[17] These were first calculated as corrections to the coefficients of the trial formula and were so given in a paper read before the American Electrochemical Society, Trans., **13**, pp. 197 et seq; 1908.

TABLE III.

Cells Set Up with Electrolytic Mercurous Sulphate Made with New Apparatus.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
*26	b_1	30	12.9	25	3.9	+ 1.44	−.039	+.0012
51	b_1	9	5.2	10	2.4	+ .15	−.009	+.0005
27	b_2	4	1.5	3	2.5	− .13	−.008	+.0006
52	b_2	15	9.2	22	3.8	+ .84	−.039	+.0001
*28	b_3	28	11.1	26	3.6	+ 1.70	−.024	+.0006
61	b_4	19	6.9	21	2.5	− .25	+.013	+.0004
62	b_5	11	7.4	16	2.2	− .05	−.006	.0000
63	b_6	10	5.6	11	2.1	− .20	−.001	+.0008
29	b_7	17	6.9	12	2.4	+ .52	−.014	+.0008
3a	b_7	8	3.2	7	2.2	− .36	+.014	+.0004
167	b_7	5	2.2	7	4.2	− .32	+.009	−.0004
168	b_7	8	3.6	10	2.2	− .08	−.012	+.0006
168a	b_7	11	6.6	15	2.7	− .44	+.018	−.0003
30	b_8	23	7.4	12	2.0	+ 1.11	−.004	+.0007
*193	b_8	42	22.9	38	5.3	+ 2.14	.000	+.0008
46	b_8	9	3.6	5	9.7	− 1.30	+.010	+.0050
46a	b_8	6	3.2	8	2.1	− .31	+.002	+.0007
*46b	b_8	30	15.8	35	9.3	+ .79	+.092	−.0051
31	b_9	11	5.8	10	2.3	+ .52	−.023	+.0004
47	b_9	6	2.6	4	2.3	− .39	−.010	+.0011
32	b_{10}	3	1.8	5	1.8	− .83	−.002	+.0010
4a	b_{10}	9	5.1	11	4.2	− .32	+.022	−.0007
33	b_{11}	11	3.8	9	1.9	+ .25	−.005	+.0006
48	b_{11}	14	6.3	9	4.0	+ .27	−.027	+.0002
34	b_{12}	11	5.1	8	3.2	+ .66	−.026	+.0010
49	b_{12}	15	9.2	19	2.4	+ .18	−.005	+.0006
6a	b_{13}	4	2.2	5	2.1	− .54	+.005	+.0006
176	b_{13}	12	4.5	12	2.5	− .36	+.008	+.0004
151	b_{14}	6	2.6	8	1.8	− .60	+.004	+.0008
152	b_{14}	6	2.1	4	1.9	− .61	+.002	+.0007
153	b_{14}	4	2.6	7	2.1	− .48	+.007	+.0004
154	b_{14}	3	1.1	2	2.1	− .15	+.004	+.0010
155	b_{14}	4	1.7	6	2.1	− .18	+.007	+.0007
156	b_{14}	4	2.3	6	2.0	− .27	+.006	+.0006
164	b_{14}	10	3.2	9	2.1	− .39	+.009	+.0010
165	b_{14}	4	2.5	8	2.6	− .62	+.014	+.0003

* Excluded in taking means.

TABLE III—Continued.

Cells Set Up with Electrolytic Mercurous Sulphate Made with New Apparatus—Continued.

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
166	b_{14}	10	5.2	10	2.4	− .29	+.017	−.0004
111	b_{14}	8	4.1	13	2.2	− .51	+.012	+.0002
113	b_{14}	7	2.5	8	1.7	− .39	+.002	+.0006
171	b_{14}	5	2.1	5	2.1	− .73	+.001	+.0008
172	b_{14}	5	2.0	5	1.6	− .64	+.004	+.0003
37	b_{15}	5	2.5	8	1.6	− .55	.000	+.0009
*15a	b_{16}	25	12.5	35	7.7	+ .76	+.050	−.0043
69	b_{17}	8	3.8	11	2.2	− .51	+.007	+.0005
59	b_{18}	7	2.6	9	1.8	− .05	+.006	+.0006
60	b_{19}	8	4.2	13	1.9	− .19	+.004	+.0006
*50	b_{20}	34	13.3	46	4.0	+ 2.97	−.016	−.0004
*53	b_{21}	18	11.2	26	3.3	+ .25	+.002	−.0004
54	b_{22}	12	7.8	13	2.4	− .14	+.001	+.0001
55	b_{23}	9	5.6	12	2.3	− .46	+.017	.0000
56	b_{24}	5	2.4	6	1.9	− .45	+.018	−.0001
57	b_{25}	8	3.1	8	2.3	+ .17	+.016	−.0002
178	b_{26}	8	3.3	12	4.2	− .34	+.032	−.0016
*P9	b_{26}	32	12.1	39	6.6	+ .08	+.076	−.0027
*P11	b_{26}	99	20.9	125	13.5	+ .33	+.177	−.0063
*P12	b_{26}	23	7.1	30	8.9	+ .37	+.069	−.0046
179	b_{27}	7	4.1	17	4.1	− .48	+.030	−.0014
187	b_{27}	6	2.4	5	1.8	− .41	+.008	+.0002
188	b_{27}	7	2.6	5	3.7	− .36	+.031	−.0016
180	b_{28}	9	2.9	8	5.9	− .09	+.046	−.0028
190	b_{29}	11	5.5	9	2.0	− .09	−.006	+.0002
191	b_{30}	9	4.9	11	1.6	− .30	+.024	−.0010
192	b_{31}	10	3.0	7	2.5	− .22	+.027	−.0011

* Excluded in taking means.

In view of the unmistakable hysteresis found in some of the cells for which the data are tabulated above, not all were included in calculating the coefficients of the final temperature formula. An arbitrary criterion for rejection was decided upon, those cells being excluded in which the mean and maximum difference with ascending and descending temperatures, taking the last measurements of each set at each temperature, exceeded 10 and 25 microvolts respectively. (Columns 4 and 5.) Even on this basis 137 cells, over two-thirds of the whole number taken, passed inspection. Among

TABLE IV.

Cells Set Up with Chemically Prepared Mercurous Sulphate.

[Results expressed in microvolts]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
86	c	3	1.3	3	1.8	− .46	−.002	+.0007
99	d_1	7	4.3	8	2.6	+ .45	−.030	+.0007
99a	d_1	10	5.9	8	1.8	+ .14	−.005	+.0005
84	d_2	7	4.4	11	1.7	− .67	+.002	+.0011
84a	d_2	4	1.9	5	1.6	− .53	+.001	+.0010
*43	e_1	30	13.5	31	5.4	+ .79	+.042	−.0026
1a	e_1	20	8.8	16	3.5	+ .82	+.007	−.0008
157	e_1	15	7.8	20	7.1	+ .39	+.067	−.0042
158	e_1	8	2.6	8	2.6	− .41	+.015	−.0002
160	e_1	9	6.2	25	1.7	− .29	+.001	+.0004
161	e_1	5	2.9	11	2.3	− .51	+.002	+.0002
162	e_1	5	1.7	8	2.5	− .41	+.012	−.0002
103	e_2	7	3.4	6	1.1	− .69	+.015	+.0008
2a	e_2	17	9.8	17	2.3	− .12	−.014	+.0012
44	e_3	14	5.8	11	5.5	+ .19	+.043	−.0029
104	e_3	4	2.1	9	1.9	− .63	+.009	+.0004
105	e_4	6	2.6	4	2.3	− .25	+.098	+.0002
106	e_5	7	2.9	8	2.0	− .24	+.004	+.0003
106a	e_5	5	1.2	3	1.7	− .41	+.010	+.0002
107	e_6	6	3.1	9	1.5	+ .23	+.097	+.0004
98	f_1	10	2.5	8	4.0	− .08	+.036	−.0021
97	f_2	4	1.1	2	2.3	− .21	+.002	+.0001
*100	g_1	56	23.6	53	7.0	+5.09	−.030	−.0011
*100a	g_1	68	37.6	66	9.2	+3.34	−.022	+.0004
*101a	g_2	127	90.6	160	11.7	+4.83	−.020	−.0020
*163	g_3	40	16.8	29	7.1	+3.06	−.044	−.0023
*95	h_1	41	21.1	46	6.5	+1.91	+.038	−.0042
*96	h_2	49	27.2	43	10.6	+3.56	+.046	−.0079
85	h_3	5	2.1	5	1.9	− .49	−.004	+.0006

* Excluded in taking means.

TABLE V.

Cells Set up With Specially Treated Commercial Samples of Mercurous Sulphate.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
93	i_1	14	5.5	8	2.6	+ .72	+.001	−.0007
94	i_2	5	1.4	3	2.1	− .19	−.006	+.0005
78	k_1	4	2.3	7	1.5	+ .18	+.012	+.0007
79	k_2	4	1.6	4	1.1	− .06	+.011	+.0006
80	k_3	4	1.6	4	1.6	− .46	+.003	+.0004
81	k_4	6	2.2	5	0.6	− .16	+.011	+.0006
82	k_5	7	3.9	8	2.2	− .09	−.002	+.0003
108	l_1	7	3.1	8	1.6	+ .72	+.010	+.0002
116	l_2	16	7.1	24	3.0	+ .23	.000	+.0002
109	l_3	6	2.2	4	1.5	+ .85	−.003	+.0007
114	l_4	6	2.8	5	2.6	+ .09	−.005	+.0002
115	l_5	5	1.7	4	1.9	+ .93	+.005	−.0001
117	m_1	8	5.1	8	2.8	+1.35	+.001	−.0006
119	m_2	8	3.2	9	2.1	.00	+.004	.0000
118	m_3	8	4.0	25	3.0	+ .22	−.001	−.0004
120	m_4	9	4.0	16	3.8	− .11	+.009	−.0005
90	n_4	7	2.2	6	2.3	+ .28	+.015	+.0003
91	n_5	6	1.8	3	1.7	+ .58	−.027	+.0004
92	n_6	6	2.1	8	2.1	+ .03	−.013	+.0008

TABLE VI.

Exchange Samples of Mercurous Sulphate.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
39	Hulett I	15	6.2	12	2.4	−.01	−.002	+.0007
141a	Hulett II	5	2.6	6	1.7	−.45	+.009	+.0003
142	"	7	3.2	7	1.5	−.20	.000	.0000
143	"	4	2.4	9	1.9	−.46	−.007	+.0008
144	"	5	3.6	14	2.1	−.35	−.011	+.0009
145	"	5	3.0	4	4.0	−.33	.000	+.0004
146	"	11	6.2	19	1.9	−.27	+.016	−.0003
147	"	5	1.9	6	1.8	−.45	.000	+.0004
148	"	8	3.5	7	1.7	+.01	−.008	+.0001
149	"	6	2.7	5	1.9	−.07	−.005	+.0001
150	"	5	1.6	5	2.9	−.59	−.034	−.0001
†169	"	5	2.2	10	1.7	−.23	−.009	+.0008
†170	"	11	7.4	18	3.3	−.15	+.028	−.0004
*189	Guthe	23	13.3	28	6.4	+.79	+.060	−.0040

* Excluded in taking means. † Clear crystal cells.

TABLE VII.

Exchange Cells.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
O_2	P.T.R.	13	7.8	12	4.3	+1.70	−.059	+.0012
*4	L.C.E.	92	37.6	108	11.6	− .43	−.158	+.0044
*6	L.C.E.	94	36.3	86	7.9	+1.01	−.180	+.0063
*H26	N.P.L.	40	25.0	46	3.1	+1.08	−.055	+.0019
*C19	N.P.L.	147	82.5	214	6.8	+2.90	−.405	+.0154
P53	N.P.L.	19	8.0	22	8.5	− .65	−.050	+.0016
*P54	N.P.L.	48	26.5	63	2.5	+ .98	−.021	+.0042
K11	N.P.L.	4	1.7	5	1.7	− .15	+.007	+.0002
K15	N.P.L.	4	1.5	5	1.4	− .21	+.005	+.0005
*H.B.9	N.P.L.	46	11.3	28	7.6	+1.70	−.070	+.0041
57	Wold	9	2.4	5	1.5	− .14	+.004	+.0011
†*O_4	Hulett	43	23.9	82	5.7	−2.58	+.016	+.0045
†A_3	Hulett	14	8.5	13	3.2	− .05	+.010	.0000
†*A_{52}	Hulett	26	12.3	28	3.1	+1.79	−.016	+.0005
†C_1	Guthe	25	9.5	20	4.7	− .63	+.023	+.0005
†*5	Carhart	19	10.6	57	4.1	+ .14	+.039	−.0014
†*8	Carhart	39	23.6	36	3.0	+1.98	−.038	+.0011
1	Strong	21	9.1	15	2.1	+ .33	+.008	+.0010
*2	Strong	31	12.8	29	5.3	+1.12	+.012	+.0007
3	Strong	15	5.7	14	2.5	− .05	+.017	+.0010

* Excluded in taking means. † Clear crystal cells.

TABLE VIII.

Cells Set Up with Different Samples of Cadmium Sulphate.

[Results expressed in microvolts.]

Cell	Mercurous Sulphate	Mean Range All Observations	Mean Range (Last Observations at Each Temperature)	Maximum Range (Last Observations at Each Temperature)	$\sqrt{\frac{\Sigma r^2}{9}}$	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
121	b_{15}	6	2.6	9	3.1	−.48	+.001	+.0006
122	b_{15}	5	2.1	7	2.1	−.61	+.011	+.0003
123	b_{15}	4	2.1	6	2.3	−.57	+.006	+.0006
124	b_{15}	10	5.4	11	2.3	−.20	−.005	.0000
125	b_{15}	11	5.6	14	2.7	+.24	−.007	−.0004
126	b_{15}	6	1.9	4	2.2	+.53	+.011	−.0002
127	b_{15}	7	4.4	10	1.9	−.50	+.007	+.0002
128	b_{15}	8	4.0	9	1.8	−.57	+.016	+.0003
133	b_{15}	10	5.5	13	2.0	+.21	−.010	+.0007
*136	b_{15}	33	16.2	44	13.8	+.46	−.106	+.0001
138	b_{15}	14	8.3	22	2.9	+.31	−.015	−.0004

* Excluded in taking means.

those excluded are 11 of the 22 cells given in Table II, in all of which relatively coarse-grained white samples of mercurous sulphate were employed; 10, including 3 portables of special construction, of the 63 of Table III, all set up with gray samples of electrolytic mercurous sulphate; 7 of the 29 cells of Table IV, nearly all set up with coarse-grained white samples of chemically prepared mercurous sulphate; 1 of the 14 cells set up with exchange samples of mercurous sulphate; 11 of the 20 exchange cells and 1 of the 11 cells of Table VIII.

The corrections to the coefficients of the trial formula were calculated from the means of the separate residuals of the 137 cells, equal weight being given to each cell. Applying the corrections thus found, we obtain

$$E_t = E_{20} - .00004075\,(t-20) - .000000944\,(t-20)^2 + .0000000098\,(t-20)^3$$

the final temperature formula in terms of which all the results are expressed.

Table IX shows the agreement of the corrections to the coefficients of the final formula, for the separate groups corresponding to Tables II to VIII inclusive, excluding the 41 cells just referred to.

Columns 3, 4, and 5 were obtained from the means of the residuals of the individual cells composing the group, as calculated from the final temperature formula, each cell being given equal weight.

TABLE IX.

Mean Corrections in Microvolts to Coefficients of Final Formula.

Table	Number of cells	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
II	11	+.15	−.007	+.0003
III	53	−.09	+.003	−.0001
IV	22	−.11	+.003	−.0001
V	19	+.36	−.002	.0000
VI	13	−.14	−.003	.0000
VII	9	+.22	−.006	+.0007
VIII	10	−.04	−.001	−.0001
II–VIII	137	+.01	.000	.0000

The agreement of mean corrections for the separate groups is excellent. Particular attention should be called to the results for the exchange cells (Table VII), which do not differ appreciably from the rest.

The agreement of the separate cells with the final temperature formula is further shown by Tables X and XI, which give respectively the mean residuals and mean deviation for each group at each temperature. The last line of each table gives the corresponding values for all the cells on which the final temperature formula is based.

TABLE X.

Mean Residuals for Each Group given by Final Temperature Formula.

[Results expressed in microvolts.]

Table	Number of cells	0	5	10	15	20	25	30	35	40
II	11	+8.4	+6.4	+4.5	+1.9	= 0	−2.0	+0.5	+1.9	−3.4
III	53	−3.7	+1.8	+2.2	−0.3		+0.9	+3.4	+6.1	+1.5
IV	22	−3.7	+2.0	+1.2	+0.4		+1.8	+4.0	+5.3	+2.5
V	19	+6.9	+9.3	+5.1	+1.8		−2.3	−1.3	−1.7	−6.8
VI	13	−1.6	+1.9	0.0	−0.3		+0.5	+2.9	+5.3	+2.9
VII	9	+9.9	+8.5	+3.2	−0.3		−1.0	−0.3	−1.0	−6.4
VIII	10	−2.4	+3.2	+0.8	−1.1		−0.1	+2.8	+3.8	+1.8
	137	−1.4	+2.4	+1.0	−1.2	−1.4	−0.7	+1.0	+2.4	−1.6

TABLE XI.

Mean Deviation of the Individual Cells from Final Temperature Formula.

[Results expressed in microvolts.]

Table	Number of cells	0	5	10	15	20	25	30	35	40
II	11	16.4	10.8	6.0	4.4	0	3.3	4.8	7.4	9.0
III	53	12.6	7.8	4.4	2.3	0	2.0	4.2	6.4	4.8
IV	22	12.4	5.2	3.0	1.5	0	2.6	4.5	5.6	4.8
V	19	8.9	9.0	5.8	2.3	0	2.8	3.7	5.8	8.4
VI	13	5.9	3.6	2.3	1.1	0	1.4	2.9	5.4	5.0
VII	9	16.9	9.1	6.2	3.4	0	3.3	5.1	5.9	7.5
VIII	10	7.5	6.9	4.0	2.7	0	2.3	4.6	5.8	5.8
II-VIII	137	11.6	7.3	4.4	2.3	0	2.4	4.2	6.1	5.9

Since all the cells of the Bureau of Standards were set up with 12.5 per cent amalgam, it seems probable that the cause of hysteresis observed in almost one-third of the whole number taken lies elsewhere. The agreement of the cells set up with large crystals of cadmium sulphate (marked † in the tables) with the remainder in which finely crushed cadmium sulphate crystals were employed, indicates that the irregularities are connected with the paste limb. This conclusion is strengthened by the behavior of the cells in which scant quantities of mercurous sulphate were employed in making up the paste. A further study of the abnormal cells will be undertaken with the object of establishing definitely the cause of their irregularities by an analysis of their ingredients, by setting up new cells to verify the conclusions which may thus be reached and by a redetermination of the temperature coefficient and behavior of amalgams, particularly at lower temperatures.

After making an analysis of the results here given, it seemed probable that the cells exhibiting hysteresis should also have shown abnormal initial values, as the laboratory temperature generally differed from 25°, the temperature of the comparing baths. An examination was therefore made of the observations on the particular cells immediately after they were set up, and in nearly every case evidence of hysteresis was indeed found. This was commented on in the paper on the Clark and Weston cells frequently referred to, where attention was called to the fact that such cells tended to approach normal values. The exceptions to this rule are nearly all found in the cells of Table V, set up with commercial samples of mercurous sulphate treated with sulphuric acid under various conditions, some of which exhibited relatively high initial values, which, however, have persisted without appreciable change. Not one of these cells shows appreciable hysteresis, indicating that the high values are probably due to residual impurities.

TEMPERATURE OF MAXIMUM ELECTROMOTIVE FORCE.

In making the first sets of measurements at 5° and 0° it was found that the temperature coefficient unmistakably changed sign between these limits, which was verified by the subsequent observations with ascending temperatures.

The differentiation of the corrected temperature formula gave + 3°.0 as the temperature of maximum electromotive force and zero temperature coefficient. Since this corresponds approximately to the temperature of saturation of the cadmium sulphate solution employed in the portable cells of the Weston Electrical Instrument Company, which have a practically negligible temperature coefficient, the solubility curve of cadmium sulphate was computed by the least squares method from the data of Mylius and Funk.[18] The observations, while not as concordant as might have been desired, ranged from −10° to +60° and led to a formula giving a minimum solubility at +1°. The very close agreement of these values has suggested further experimental work which it is hoped can shortly be undertaken.

THE BEHAVIOR WITH RAPID TEMPERATURE CHANGES.

In March, 1907, some preliminary measurements were made on over 90 cells contained in one of the baths to determine the influence of relatively rapid temperature changes. The temperature was reduced from 25° to 20° in 2½ hours, and while the temperature was falling the difference between 7 of the cells connected in series and 7 of the reference cells contained in another bath was measured. In addition, one partial and three complete sets of observations were made on the separate cells while at the lower temperature, at which they were left for several weeks. The temperature was then rapidly increased to 25° and three further observations made, the first within two hours. Additional observations on a number of normal cells transferred back and forth from the 25° bath to the 20° bath showed that, even with very abrupt changes in temperature, most of the cells reached a practically constant value well within an hour, with ascending temperatures. On lowering the temperature a longer time was required for the attainment of the normal values.

It was found that nearly all the cells agreed quite as well at 20° within 24 hours after the temperature was changed as at 25°; that the corresponding difference in electromotive force was approximately 20 microvolts greater than that given by the formula of Jaeger and Wachsmuth, and that nearly all the cells assumed their

[18] Ber., **30**, p. 824; 1897.

normal values within 24 hours after they were brought back to 25°. The series observations, made while the temperature was being changed and since reduced by the new formula above proposed, show further that the mean value of the 7 cells selected agreed with the calculated values to within ten microvolts, even though the temperature was changed at the rate of 2°.5 per hour.

In December, 1907, further preliminary measurements were made over a wider range on 7 other cells selected as representative. They were first separately transferred from a 25° bath to another regulated at 4°.8. The results are given in the curves of Fig. 1, in which the differences between the individual cells and the values calculated by the proposed formula are given. From these it will be seen that one of the cells showed considerable hysteresis, while the remainder practically attained their normal values within 5 hours after an abrupt change in temperature of over 20°.

Five further sets of observations on the same cells were made under the following conditions:

While bringing the cells back to 25°, Curve 2, Fig. 2.

While changing the temperature from 25° to 35°, Curve 3, Fig. 2.

While changing the temperature from 35° to 25°, Curve 4, Fig. 2.

While changing the temperature from 25° to 20°, Curve 5, Fig. 2.

While changing the temperature from 20° to 25°, Curve 6, Fig. 2.

As will be seen from Fig. 2, in which the ordinates represent the departure of the mean values of the 7 cells from the proposed formula, the differences are mainly due to the rapidity with which the temperature was changed, as indicated by the rapid approach to normal values as soon as the heating or cooling was interrupted. The agreement with ascending temperatures was somewhat better than with descending temperatures, which was also found to be the case in the subsequent measurements made to determine the temperature formula.

The departures of the individual cells from the proposed formula are given in Table XII, which shows that one of them, No. 73, exhibited considerable hysteresis. This would of course partly account for the magnitude of the mean departure of the 7 cells (Curves 2 to 6).

TABLE XII.

Departure of Individual Cells from Final Temperature Formula.

[Results expressed in microvolts.]

Date	Temperature	Hours at Temperature	W 73	W 57	W 103	W 78	W 27	W 119	W 89	Mean
*Dec. 3.	25°		− 1	0	− 1	− 1	− 1	- 1	− 2	− 1
*Dec. 5.	25°		+ 1	0	0	+ 1	0	0	− 4	0
Dec. 5, 5 P. M.	4°8	2	+60	−9	− 1	−22	+18	−26	−13	+ 1
Dec. 5, 8.30 P. M.	4°8	5½	+54	−7	+ 3	+ 1	+17	− 3	+11	+11
Dec. 5, 10 P. M.	4°8	7	+55	−5	+ 3	+ 2	+16	− 1	+12	+12
Dec. 6, 9 A. M.	4°8	18	+45	−6	+ 2	+ 7	+13	+ 3	+11	+11
Dec. 6, 4 P. M.	4°8	25	+43	−8	0	+ 6	+10	+ 1	+ 9	+ 9
Dec. 7, 9 A. M.	4°8	42	+40	−5	0	+ 6	+10	+ 1	+10	+ 9
Dec. 7, 4 P. M.	25°	½	0	0	− 1	+ 8	0	+ 4	+10	+ 3
*Dec. 9, 9 A. M.	25°	41½	0	−1	0	+ 1	0	+ 1	+ 5	+ 1
Dec. 9, 4.20 P. M.	35°	½	− 7	0	0	− 1	0	− 1	+ 4	− 1
Dec. 10, 9 A. M.	35°	17	− 4	−2	− 2	− 8	− 1	− 2	+ 2	− 2
Dec. 11, 9 A. M.	35°	41	− 2	−2	+ 1	− 6	+ 1	0	+ 1	− 1
Dec. 11, 12.20 P. M.	25°	1	+55	0	+10	− 6	+19	+ 2	+ 2	+12
Dec. 11, 1.05 P. M.	25°	2	+53	0	+10	− 4	+17	+ 3	+ 2	+12
Dec. 11, 4 P. M.	25°	5	+47	0	+10	− 2	+15	+ 5	+ 2	+11
Dec. 11, 8 P. M.	25°	9	+41	0	+ 9	− 2	+13	+ 5	0	+ 9
Dec. 12, 10 A. M.	25°	23	+32	−4	+ 8	− 2	+ 8	+ 3	0	+ 6
Dec. 12, 4 P. M.	25°	29	+31	−4	+ 8	+ 1	+ 6	+ 3	+ 1	+ 7
Dec. 13, 11 A. M.	25°	48	+29	−6	+ 7	− 1	+ 7	+ 1	− 1	+ 5
Dec. 13, 1.15 P. M.	20°	1½	+59	−6	+ 6	−11	+13	− 3	− 4	+ 8
Dec. 13, 4.25 P. M.	20°	3½	+55	−6	+ 6	− 6	+ 8	− 2	− 4	+ 7
Dec. 14, 9 A. M.	20°	20	+42	−7	+ 2	− 4	+ 5	+ 2	− 4	+ 5
Dec. 14, 4.15 P. M.	20°	27	+40	−8	+ 1	− 3	+ 5	− 2	− 4	+ 4
Dec. 16, 9 A. M.	20°	68	+33	−7	+ 1	− 1	+ 3	0	− 4	+ 4
Dec. 16, 12.09 P. M.	25°	4 min	+24	−3	+ 3	+ 4	+ 1	+ 4	− 2	+ 4
Dec. 16, 12.27 P. M.	25°	22 min	+25	−2	+ 4	+ 4	+ 1	+ 3	− 2	+ 5
Dec. 16, 1 P. M.	25°	51 min	+25	−3	+ 4	+ 4	+ 2	+ 2	− 2	+ 5
Dec. 17, 4.30 P. M.	25°	28 hrs	+24	−4	+ 4	+ 3	+ 2	+ 1	− 2	+ 4

*Taken as basis of reference.

The results obtained in the preliminary measurements above described indicated the advisability of keeping the cells at least 24 hours at each temperature employed in the determination of the temperature formula, even though a much shorter period would have been sufficient for most of them.

RESULTS OBTAINED BY OTHER INVESTIGATORS.

A brief outline of previous work on this subject has been given above, and it therefore only remains to compare the results obtained with those found in this investigation. Since the results obtained by Dearlove, Barnes, and Barnes and Lucas are quite irregular and indicate the existence of large hysteresis effects as has been pointed out above, this discussion will be confined to a comparison of those obtained at the Reichsanstalt and at the Bureau of Standards.

The original measurements by Jaeger and Wachsmuth,[19] upon which the generally accepted formula is based, were therefore reduced by the author, and it was found that if the obervations at 0°, 1.5°, and 1.7° were excluded the average deviation of the measurements from the new formula amount to ±13 microvolts as compared with ±8 microvolts by the generally accepted formula. When it is recalled that the results of Jaeger and Wachsmuth were obtained from a relatively small number of measurements on four cells, set up with 1 : 6 amalgam, and that no attempt was made to maintain the temperature at a constant value for any length of time, the agreement is quite remarkable. The exclusion of the observations at the lower temperatures, at which the differences from the proposed formula are from 100 to 200 microvolts, is fully justified by Jaeger's admission of the existence of irregularities below 10° for the 1 : 6 amalgam.

As pointed out in the introduction to this paper, the results obtained by Jaeger in 1898 also apply to cells with amalgam of the same composition, and further establish the existence of irregularities at lower temperatures. The differences between individual cells of the same lot indicate, however, that the abnormal values may not be entirely due to the 1 : 6 amalgam.

The results obtained by Jaeger and Lindeck[20] in 1899–1901 have also been carefully worked over. No particular attention was paid to the eight old cells with 1 : 6 amalgam, six of which were

[19] Wied. Ann., **59**, p. 575; 1896.

[20] Ann. d. Phys., **5**, p. 1 (1901). Zs. Instk., **21**, p. 33–65 (1901).

among those previously reported as abnormal. The 56 series of measurements on twelve new cells with 13 per cent amalgam were first tabulated. The two series at 0°, extending over two periods of 8 and 11 days, show relatively large differences between the individual cells, as well as a not inconsiderable hysteresis. Instead of taking the mean of all such measurements, the mean of the last three in each series was taken. Series 15 and 54 were also excluded on account of relatively sudden temperature changes. The observations were otherwise grouped in the same manner as was done by Jaeger and Lindeck, and from these the mean values of the twelve cells at twelve temperatures in the range 0° to 30° were obtained. The mean deviation from the Reichsanstalt formula was found to be ±40 microvolts, while the mean deviation from the formula here proposed amounted to ±20 microvolts. This suggested the desirability of computing a temperature formula from the Reichsanstalt results. It was found that the mean values of the twelve cells, the observations grouped as above, could best be expressed by the formula

$$E_t = E_{20} - .00003988\,(t-20) - .000000941\,(t-20)^2 + .0000000146\,(t-20)^3$$

with a mean residual of ±10 microvolts. In addition, the coef ficients are in excellent agreement with those of the temperature formula proposed.

The results of further measurements made on five cells set up at the same time and with the same material as the twelve to which the above results apply, together with those obtained with two new lots of 20 each, set up with respectively 12 per cent and 13 per cent amalgams, are given in Table XIII. The cells were only measured at 0°, at which they were kept for several days, and at room temperatures. The b and β groups were freshly set up and changed considerably between the measurements at room temperatures, made before and after the observations at 0°, so that the differences between 0° and 20° were calculated on the assumption that the rate of change was uniform in the interval.

TABLE XIII.

Summary of Results—Jaeger and Lindeck.

Cells	Number	Amalgam Per cent Cadmium	Mean Difference in Microvolts 0°–20°
a_1–a_5 a_{11}–a_{17}	12	13	318
a_6–a_{10}	5	13	230
b_1–b_{15}	15	13	433
b_{16}–b_{20}	5	13	379
β_1–β_5	5	12	345
β_6–β_{20}	15	12	355
All	57	—	358

The agreement of the individual cells as well as the separate groups is not entirely satisfactory and hardly establishes the existence of a difference in the mean temperature coefficient between 0° and 20°, arising from the employment of 12 and 13 per cent amalgams. The mean difference in value between 0° and 20° for the 137 cells, all set up with 12.5 per cent amalgam, on which the proposed formula is based, is 359 microvolts, while that given by the formula of Jaeger and Wachsmuth is 500 microvolts, so that it may safely be concluded that the heretofore accepted formula can not be applied beyond the limits, 10°–30°, indicated by Jaeger.

Since the meeting of the American Electrochemical Society last April, at which this paper was first presented, there have appeared two short papers on "The Cadmium Cell at Low Temperatures" by Henry Tinsley,[21] and on "The Influence of Temperature on the Electromotive Force of Cadmium Cells," by R. Jouast.[22] Tinsley reports on some observations made on a number of cells set up in accordance with the specifications of the National Physical Laboratory, containing 12.5 per cent amalgam and agreeing within 5 parts in 100,000 with the cells of the National Physical Laboratory.

[21] London Electrician, **61**, p. 321; June 12, 1908.
[22] C. R., 147, 42; July 6, 1908.

During a severe cold spell last winter a difference of nearly 2 millivolts was observed between these and a master cell, of considerably larger size, containing 10 per cent amalgam, although the former agreed well with one another. One of them was therefore selected and measured against the master cell, both being placed in an oil bath, the temperature of which was allowed to rise from 3° to 21°. The differences between the two cells, amounting to nearly 2 millivolts at 3°.2, are attributed by Tinsley to the amalgam, the cell with 12.5 per cent giving lower values at the lower temperatures.

Jouast, at the Laboratoire Central d'Électricité, found that cells containing 12.5 per cent amalgam gave a value at 0° 100 microvolts less than that given by the formula of Jaeger and Wachsmuth, but agreeing with the results of this investigation. On the other hand, cells with 10 per cent amalgam, while agreeing with each other at 10°, differed at 0° by several parts in 10,000 among themselves and had values 1 millivolt higher than the 12.5 per cent cells. On abrupt cooling, the electromotive force increased almost instantly by approximately 2 millivolts, the cells attaining a constant value after several days. The abnormal behavior is again attributed to the composition of the amalgam, but while Tinsley finds this to occur with the 12.5 per cent amalgam, Jouast finds irregularities with the 10 per cent amalgam. The author found only a few of the entire 200 cells employed, all of which were set up with 12.5 per cent amalgam, which differed by more than 50 microvolts from the temperature formula proposed, so that it appears quite probable that the irregularities are not due to the amalgam.

In Table XIV are given the differences in E. M. F. calculated by the various formulæ, for every 5° from 0° to 40°, in terms of the value at 20° taken as standard.

From the table it will be seen that the agreement of all the formulæ is very good between 10° and 30°. In work of the highest precision, however, the differences, amounting to 20 microvolts in the interval 20° to 25°, between the generally accepted formula and that proposed may have to be taken into account.

TABLE XIV.

Differences in Microvolts from 20° Value by the Various Formulæ.

Temp.	Jeager and Wachsmuth	Jaeger and Lindeck *	Smith	Wolff
0	+ 500	+ 304	+ 505	+ 359
5	+ 424	+ 337	+ 428	+ 366
10	+ 315	+ 290	+ 319	+ 304
15	+ 174	+ 174	+ 176	+ 179
20	0	0	0	0
25	— 206	— 221	— 209	— 226
30	— 445	— 478	— 451	— 492
35	— 716	— 761	— 725	— 791
40	—1020	—1057	—1033	—1114

*Computed by author.

SUMMARY OF CONCLUSIONS.

From the results obtained in this investigation the following conclusions may be drawn:

1. That Weston cells can be set up which exhibit extremely little hysteresis in the range 0° to 40°, even when subjected to large and rapid temperature variations.

2. That such cells will maintain their values under prolonged heating or cooling.

3. That the relation between E. M. F. and temperature is best represented by the formula

$$E_t = E_{20} - .00004075\,(t - 20) - .000000944\,(t - 20)^2 + .0000000098\,(t - 20)^3.$$

4. That no indications were found of differences arising from the methods of preparation of the mercurous sulphate employed.

5. That the results of Jaeger and Lindeck on cells with 12 and 13 per cent amalgams are in better agreement with the formula given above than with the generally accepted temperature formula, which, however, agrees fairly well with the former between 10° and 30° C.

6. That some of the cells showed marked and persistent hysteresis, particularly at lower temperatures for which the values are in general greater than those corresponding to the formula above given.

7. That the majority of cells in which hysteresis was found were set up with relatively coarse-grained white samples of mercurous sulphate.

8. That a similar behavior was found in most of the cells having abnormal values at room temperatures, and in cells in which oil had been admitted through defective seals.

9. That nearly all the cells exhibiting abnormal initial values showed evidence of decided hysteresis.

10. That according to the above formula the E. M. F. of the Weston cell has a maximum value at 3°, corresponding approximately to the temperature of minimum solubility of cadmium sulphate, and to the saturation temperature of the cadmium sulphate solution employed in the portable cells of the Weston Company for which the temperature coefficient is almost negligible.

The author wishes to acknowledge the valuable assistance given him by Mr. M. P. Shoemaker and Mr. J. H. Dellinger in making about half of the observations, and to thank Mr. Shoemaker for the regulation of the baths and for his painstaking labors in the computation of the results.

WASHINGTON, September 1, 1908.

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